Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 82 (2015) 908 – 914

Energy Procedia

ATI 2015 - 70th Conference of the ATI Engineering Association

Model of a chemical looping process for hot gas desulfurization in power plants.

Jessica Settino[a]*

[a]University of Calabria, Via P.Bucci, Arcavacata di Rende 87046, Italy

Abstract

A mathematical model of a transport reactor has been developed and implemented with the software Athena Visual Studio. The one-dimensional, steady state model takes into account kinetics and hydrodynamic effects. The reactor has been divided into three zones: the acceleration zone, the fully developed zone and the exit zone. Empirical correlations are used to describe the different regions, with particular reference to the axial voidage profile. The unreacted shrinking core model with variable effective diffusivity is applied to determine the sorbent conversion and the reaction rate. Two different sorbents were investigated: zinc titanate, considered as one of the most promising mixed metal oxide and calcium oxide as natural material. The differences, in terms of operating temperature and desulfurization efficiency, are discussed. Finally, to estimate the advantages of the described alternatives, they have been included in an Integrated Gasification Combined Cycle (IGCC) and simulated by the software package Thermoflex. The results show an interesting enhancement of the efficiency up to 3% accompanied by a simpler system configuration.

Peer-review under responsibility of the Scientific Committee of ATI 2015

Keywords: hot gas desulfurization; transport reactor; kinetics; hydrodynamic; efficiency

1. Introduction

Gasification of coal with air or oxygen produces so called syngas or producer gas, mainly composed of H_2, CO, CO_2, H_2O, CH_4 and various contaminants such as NH_3, H_2S and COS. In order to use the syngas for the electricity production without harming the downstream technologies and the environment, removal of sulfur compounds is necessary. Amine-based absorption processes are currently considered as state-of-the-art. In spite of their excellent desulfurization efficiency, this strategy is thermally inefficient, since it requires the gas to be cooled below the dew point and then reheated downstream. Thus, alternative

* Corresponding author. Tel.: +39 340 163 0239; fax: +039 0984 494673.
E-mail address: jessica.settino@unical.it

Peer-review under responsibility of the Scientific Committee of ATI 2015
doi:10.1016/j.egypro.2015.11.838

solutions, operating at higher temperature, would be interesting in order to avoid gas cooling and the related heat exchangers. A review of the most used methods for hot gas desulphurization (HGD) is available in [1], where both *in situ* and external sulphur capture are discussed. This work is focused on the external desulphurization and in particular, on the analysis of a chemical looping process and its effect on the overall power plant performance. A proper model is necessary in order to obtain reliable results. Because of the relatively recent application of chemical looping for HGD, an accurate description of the process in commercial software is not available. Thus, a numerical approach has been used and a model of a transport reactor has been developed and solved in the Athena Visual Studio software.

Nomenclature

A	reactor cross sectional area (m^2)
a_v	external particle surface area per unit reactor volume (m_s^2/m_r^3)
b	moles of reacted sorbent per mole of gas
C_p	heat capacity (J/(mol K)
n	molar flow rate (mol/s)
h	gas-solid heat transfer coefficient (W/(m^2 K))
ΔH	enthalpy of reaction (J/mol)
R	reaction rate (mol/(kg_s s))
T	temperature (K)
z	axial coordinate (m)
ε	bed voidage
ρ	density (kg/m^3)

Subscript

s	solid
g	gas

2. Chemical looping desulfurization

Chemical looping has gained in few decades increasing attention of the scientific community. This is also due to the wide range of applications [2]. From a general point of view, a regenerative solid sorbent circulates alternatingly between two reactors. In this specific case, using chemical looping for hot gas desulfurization, the sorbent, usually a metal oxide, is brought in contact with the syngas and is converted into its sulfide. In the next step, the sorbent is regenerated with air so as to restart the cycle. The system consists therefore of two reactors: the regeneration and the desulfurization reactor. In this work, the chosen reactor type is a transport reactor, i.e. a riser.

Many authors have been performing thermodynamic calculations in order to determine the most suitable metal oxide sorbents. From the studies of Westmoreland [3] the most promising ones turned out to be Zn, Cu, Fe, Mo, Ba, Ca, Mn. Every sorbent has its own advantages and limitations which can be overcome by adding a supporting material, so as to limit sorbent degradation by increasing the mechanical stability. According to Elseviers [4], zinc-based sorbents, and among them mainly zinc titanate (Zn_2TiO_4,), are the most effective for intensive desulfurization, allowing low residual H_2S concentration of the order of few ppm to be reached at temperature of 500-650°C. Due to its properties, zinc titanate will be used in the developed model.

A rather cheap alternative is represented by CaO based sorbents, stable in a temperature range of 800-1200°C. Due to the operating temperature, typical for many gasifiers, CaO is usually added directly to the gasification chamber for an *in situ* desulphurization. Studies performed by Jagtap [5] and recently by Ju Wang et al. [6] evaluate sorbent regeneration in order to use it in a chemical looping process.

3. Model description

The transport reactor was assumed to be adiabatic, steady state and one dimensional. Both solid and gas phase hydrodynamics are considered as plug flow. To determine the concentration profile of the syngas components, along the reactor, the mass and energy balance for both phases are solved within Athena Visual Studio software. The following equations describe the heat and mass balances for both phases:

$$dn_s/dz = \mathrm{b}\ \mathrm{R}\rho_s A(1-\varepsilon) \tag{1}$$

$$dn_g/dz = \mathrm{R}\rho_s A(1-\varepsilon) \tag{2}$$

$$n_s C_{ps}\, dT_s/dz = \Delta H\ R\rho_s A(1-\varepsilon) - \mathrm{h}\ (T_s - T_g) a_v\ A \tag{3}$$

$$n_g C_{pg}\, dT_g/dz = \mathrm{h} a_v A(T_s - T_g) \tag{4}$$

3.1. Kinetics

To determine the reaction rate, different models are available in literature. In spite of the great variety they are actually following two tracks: the grain model or the shrinking core. The latter, proposed by Yagi and Kunii [7], was applied to zinc titanate and modified by Konttinen et al. [8], introducing a variable effective diffusivity to consider the structural changes of the sorbent. The grain model, instead, has been described by Szekely [9] and later modified by Ranade and Harrison [10] to include property variation as a consequence of both reaction and sintering effect. In this work, the modified version of the shrinking core model discussed by Konttinen et al. [8] has been used. In spite of its simplicity, it allows to reproduce experimental results with good accuracy, ensuring the possibility to easily include the model into power plant simulations because of the low computational time required.

3.2. Hydrodynamics

Experimental evidence suggests that the solid fraction is not constant along the reactor. This aspect has been investigated by many authors and a detailed review is available in [11]. It is possible to distinguish three regions: acceleration, fully developed and exit zone. In order to model the reactor, these zones should be properly described. In this work, the empirical correlations proposed by Shadle [12–14] have been implemented, obtaining the voidage profile shown in Fig.1 for different solid mass flux.

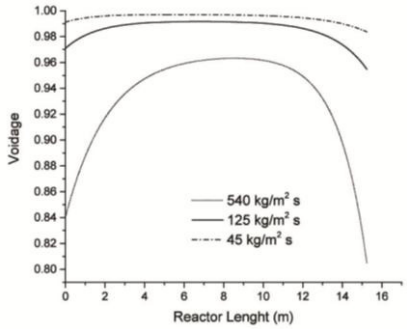

Fig. 1. Voidage profile along the reactor for a gas flow rate of 0,087 m^3/s at a pressure of 2 MPa.

The C-shape profile, evident in fig. 1, is typical of reactor with abrupt exit.

4. Results and discussion

On the basis of the described model, the performance of gas desulfurization in a riser has been analysed. The operating conditions have been assumed to be pressure of 2.0 MPa and temperature of 550°C.

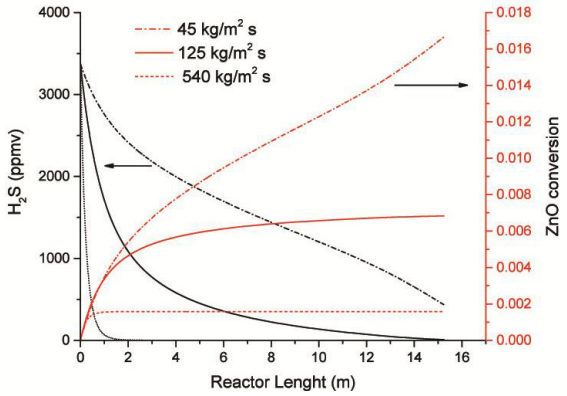

Fig. 2. H_2S concentration and ZnO conversion along the reactor for solid mass flows of 45, 125 and 540 kg/m^2 s, at a pressure of 2 MPa, a temperature of 550°C and incoming H_2S concentration of 3400 ppm.

Fig. 2 underlines the strong influence of the solid flux on both H_2S concentration and ZnO conversion. It can be noted that decreasing the solid mass flux, ZnO conversion increases. This result is expected since the sorbent conversion is proportional to H_2S concentration, which is actually higher along the reactor when the amount of sorbent introduced decreases. For low amount of sorbent flux, as observed by Monazam and Shadle [13], H_2S cannot be removed until the desired levels. It is also interesting to see that the sorbent conversion is lower than 2% in all cases. The situation is different for an efficient use of calcium oxide. If it is used as a non-regenerative sorbent, for an *in situ* desulfurization, a high sorbent conversion is required. As underlined by Fenouil [15], CaO reaction is limited by thermodynamic equilibrium. For typical gasification conditions, the H_2S concentration at equilibrium is around 300 ppm, not enough to satisfy the requirements. Thus, an external desulfurization process has to be added. A detailed economic analysis would be necessary in order to evaluate the two solutions: intensive external desulfurization with zinc titanate or *in situ* CaO for bulk H_2S removal followed by zinc titanate absorption

of residual H_2S. In the former case, the main cost is represented by the sorbent, whilst in the latter, the cost will depend on the amount of zinc titanate still needed but also on the disposal problems of the large quantities of CaS produced, which is not stable at ambient conditions. A univocal answer is difficult to find, as it depends on the H_2S final concentration required and the gasification conditions, which strongly affect the inlet H_2S concentration in the riser and thus the reaction rate. Fig. 3 (a) shows how, for the same amount of solid flux, the reaction rate decreases at lower H_2S initial values. On the other hand, to obtain the same H_2S emission at the riser outlet, for an initial value of 300 ppm compared to the other ten times higher, the required zinc titanate is lower than the 40%, as fig. 3(b) shows.

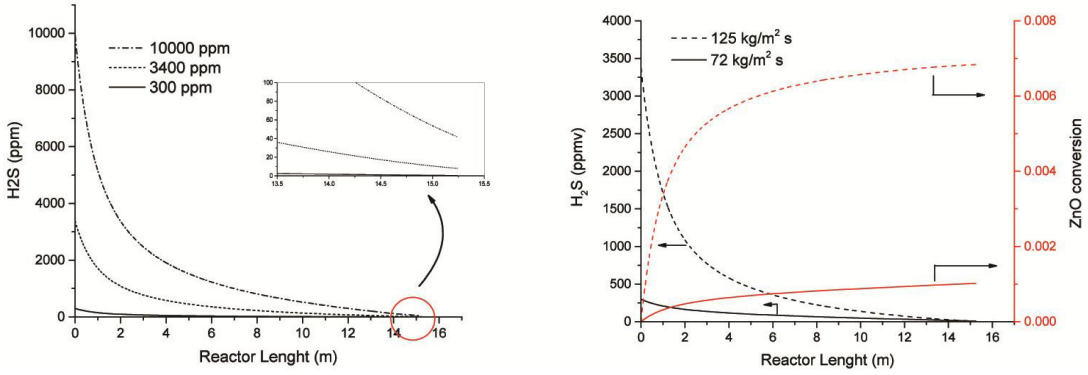

Fig. 3. (a) shows the H_2S concentration for an initial value of 300, 3400 and 10000 ppm with a constant solid flux of 125 kg/(m^2 s); (b) shows the H_2S concentration and the sorbent conversion along the reactor for an incoming concentration of 300 and 3400 ppm and solid mass flux respectively of 72 and 125 kg/(m^2 s) in order to have the same H_2S exit concentration.

5. Chemical Looping application to an Integrated Gasification Combined Cycle.

An integrated gasification combined cycle (IGCC) power plant has been simulated with the software package Thermoflex in order to investigate the difference between cold and hot gas desulfurization (CGD vs. HGD). The two systems have been compared, showing a reduction of coal needed for the same gas turbine power production, as well as an increase of the overall efficiency of about 3.5%. The enhanced efficiency is due to both increased hot gas efficiency and the more efficient heat recovery at low pressure (LP), where heat losses due to steam consumption for the acid gas removal unit (AGR) are avoided, (see Table 1). These results are in agreement with that obtained by Giuffrida [16].

Table 1. Results of simulations

Analyzed case studies	CGD	HGD
Net fuel input [MW]	371,6	339,5
Net electric efficiency[%]	43,4	47
Steam Turbine (LP) [MW]	38,2	39,98
Steam Turbine (HP) [MW]	28,8	24,9

6. Conclusions

Chemical looping is a promising technology to increase the efficiency of IGCC plants and fulfill at the same time the more and more stringent regulation about pollutant emissions. Particularly, the aim to

remove sulfur to avoid corrosion phenomena in the gas turbine and to respect the limiting values for emissions can be pursued through the chemical looping technology, ensuring high removal efficiency, less complex power plant and an increase of 3.5% of the overall efficiency. Further investigation is needed in order to evaluate the possibility of using chemical looping in a second step after the *in situ* gasification.

Acknowledgements

This work is supported by a co-financed grant from the European Commission, the European Social Fund and Calabria Region. The author would like to thank Prof. Mario Amelio, from University of Calabria, and Dr. Tilman Schildhauer, from Paul Scherrer Institut, for their precious guidance and support. The author is also grateful to Professors F. Di Maio and A. Di Renzo, for their valuable comments and suggestions.

References

[1] X. Meng, W. de Jong, R. Pal, A.H.M. Verkooijen. In bed and downstream hot gas desulphurization during solid fuel gasification: A review. *Fuel Process. Technol.* 2010; **91**:964–981.

[2] J. Adanez, A. Abad, F. Garcia-Labiano, P. Gayan, L.F. de Diego. Progress in Chemical-Looping Combustion and Reforming technologies. *Prog. Energy Combust. Sci.* 2012; **38**: 215–282.

[3] P.R. Westmoreland, D.P. Harrison. Evaluation of Candidate Solids for High Temperature Desulfurization of Low-Btu Gases. *Environ. Sci.* 1976; **10**:659–661.

[4] W.F. Elseviers, H. Verelst. Transition metal oxides for hot gas desulphurisation. *Fuel* 1999; **78**: 601–612.

[5] S.B. Jagtap, T.D. Wheelock. Regeneration of Sulfided Calcium-Based Sorbents by a Cyclic Process. *Energy & Fuels.* 1996; **10**: 821–827.

[6] J. Wang, J. Guo, R. Parnas, B. Liang. Calcium-based regenerable sorbents for high temperature H_2S removal. *Fuel* 2015; **154:** 17–23.

[7] S. Yagi, D. Kunii. Studies on combustion of carbon particles in flames and fluidized beds. *Symp. on Combustion* 1955¸ **5**: 231–244.

[8] J. Konttinen. Hot gas desulfurization with zinc titanate sorbents in a fluidized bed. 1. Determination of sorbent particle conversion rate model parameters. *Ind. Eng. Chem. Res.* 1997; **36**: 2332–2339.

[9] J. Szekely, J.W. Evans, H. Sohn. *Gas-Solid Reactions*, Accademic Press: New York, 1976.

[10] P. Ranade, D. Harrison. The variable property grain model applied to the zinc oxide-hydrogen sulfide reaction. *Chem. Eng. Sci*. 1981; **36**: 1079–1089.

[11] F. Berruti, T.S. Pugsley, L. Godfroy, J. Chaouki, G.S. Patience. Hydrodynamics of circulating fluidized bed risers: A review. *Can. J. Chem. Eng*. 1995; **73**:579–602.

[12] E. Monazam, L. Shadle. Analysis of the acceleration region in a circulating fluidized bed riser operating above fast fluidization velocities. *Ind. Eng. Chem. Res.* 2008; **47**: 8423–8429.

[13] E.R. Monazam, L.J. Shadle. Fuel gas clean-up in a transport reactor: Model development and analysis. In 18th Proc. Int. Conf. on Fluidized Bed Combustion, ASME 2005; 409–416.

[14] E.R. Monazam, L.J. Shadle, D. a. Berry. Modeling and analysis of S-sorption with ZnO in a transport reactor. *Chem. Eng. Sci.* 2008; **63**: 2614–2623.

[15] L.A. Fenouil, S. Lynn. Sorption Systems: Grain-Model Kinetics for Hot Coal-Gas Desulfurization with Limestone. *Ind. Eng. Chem. Res.* 1996; **35**: 1024–1043.

[16] A. Giuffrida, M. Romano, G. Lozza. Thermodynamic assessment of IGCC power plants with hot fuel gas desulfurization, *Applied. Energy.* 2010; **87**: 3374–3383.

Biography

Settino Jessica graduated with a Master degree in Energy Engineering. She is currently a Ph.D student at the Department of Environmental and Chemical Engineering, University of Calabria. In 2014, she has collaborated with Paul Scherrer Institut. The main areas of research interest are syngas desulphurization, power generation, clean coal technologies.